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Inclusion of mean-field spin–orbit effects based on all-electron two-component spinors: Pilot calculations on atomic and molecular properties

Miroslav Iliaš[a] and Vladimír Kellö
Department of Physical Chemistry, Faculty of Sciences, Comenius University, Mlynská Dolina, SK–842 15 Bratislava, Slovakia

Lucas Visscher
Division of Chemistry, Faculty of Sciences, Vrije Universiteit Amsterdam, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands

Bernd Schimmelpfennig
Laboratory of Theoretical Chemistry, Department of Biotechnology, Royal Institute of Technology, Teknikringen 30, S-10044 Stockholm, Sweden

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An implementation of a two-component all-electron ($jj/\omega\omega$) treatment of both scalar and spin–orbit relativistic effects in the MOLFDIR program suite is presented. Relativity is accounted for by Douglas–Kroll transformed one-electron operators: scalar (spin-free) and so called mean-field spin–orbit terms. The interelectronic interaction is represented by the nonrelativistic Coulomb operator. High-level correlated calculations of properties of several systems (FO, ClO, Cl, O_2^+, O_2^-, Tl, and TlH) where spin–orbit effects play a dominant role are presented and compared with other data. Agreement with Dirac–Coulomb(–Gaunt) reference values is in general very good. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1413510]

I. INTRODUCTION

It is known that an accurate theoretical determination of properties for systems containing heavy elements requires inclusion of both relativistic and correlation effects in electronic structure calculations.[1–5] Rigorous methods including relativity in quantum chemical calculations start usually from the four-component Dirac–Coulomb (DC), Dirac–Coulomb–Gaunt (DCG) or Dirac–Coulomb–Breit (DCB) Hamiltonian.[6] The electronic correlation treatment is based on four-component spinors (four-spinors)[3,7–9] in that case. However, these approaches are still computationally demanding and can be applied only on small and medium sized systems. They serve as a reference for other approximations of relativistic effects in molecular calculations.

In quantum chemistry, two-component relativistic approaches are the standard way of treating relativity.[2–5] In these methods, one avoids explicit representation of the small components of the four-spinor via an approximate decoupling of the electronic and positronic levels of the Dirac equation. This allows to discard the positronic solutions which are not of interest for chemical applications. An important advantage is that one can easily separate a two-component Hamiltonian into a scalar (spin-free) and spin-dependent part, allowing a quasi one-component treatment similar to nonrelativistic theory.

Other approaches including both scalar and spin–orbit relativistic effects are used within pseudopotential methods (see, e.g., Ref. 10, and references therein), or within density functional theory (DFT), either in a two-[11,12] or in four-component[13] manner.

The Douglas–Kroll (DK) transformation of the DCB Hamiltonian[14–17] results in all-electron scalar and spin–orbit operators that are bounded from below and are thus suitable for variational calculations. Of these operators the spin-free one-electron part preserves the (nonrelativistic) point-group symmetry and requires only modification of one-electron atomic integrals. Restriction to this part of the DK Hamiltonian is common and has made the DK approach the most widely relativistic approach in quantum chemical calculations.[18,19]

When spin–orbit effects are to be included the spin–orbit operator is applied usually at the post-one-component HF step[5,20–26] to couple multiplets with different spin and space symmetries. This is done either by a quasidegenerate perturbation theory (QDPT) where configuration interaction (CI) or MCSCF states are taken as zero-order wave functions (so-called LS coupling) or by an intermediate coupling scheme in spin–orbit CI (SO-CI) or by fully variational treatment of spin–orbit coupling in configuration space.[22,25]

For the scalar relativistic effects, it is usually sufficient to deal only with the one-electron term and neglect the two-electron scalar contribution.[16,17] However, this does not hold for the spin–orbit Hamiltonian, where the one- and two-electron terms cancel each other to a large extent so that both have to be included.[5,20] This complicates practical calculations because evaluation of the numerous two-electron many-center spin–orbit integrals is costly.[20]

Recently, this disadvantage has been overcome by intro-

[a]Permanent address: Department of Informatics, Faculty of Management Science and Informatics, University of Žilina, Campus Prievidza, Bakalárska 2, SK-97101 Prievidza, Slovakia.

ducing a pseudo one-electron Fock-type spin–orbit operator [called the mean-field operator (MFSO)] which is derived from the full atomic spin–orbit Hamiltonian.[26–30] This effective one-center operator together with the DK scalar term has demonstrated to work very well for a variety of systems. In these calculations the spin–orbit coupling was introduced after the orbital generation step via the QDPT or the SO-CI. In this paper we study the inclusion at an earlier stage by applying a two-component Hartree–Fock procedure in which both scalar relativistic and spin–orbit effects are taken into account. We believe that this approach (denoted here as DK +MFSO; for more details see the third section of this work) will cover a substantial part of relativistic effects and may lead to shorter expansions at the correlated stage because the effect of the spinor relaxation is already taken into account in the generation of the orbitals.

In this work both scalar and spin–orbit relativistic terms are employed variationally in the all-electron HF-SCF procedure. *JJ* coupled self-consistent field calculations are then followed by coupled cluster calculations. We applied the method for systems which properties are influenced by spin–orbit effects and for which other theoretical and experimental results are available. Further details on used methods and on studied systems follow in the next two sections.

II. THEORY

The total no-pair electronic Hamiltonian employed by us contains the one-electron spin-free Douglas–Kroll (DK) term, the mean-field spin–orbit (MFSO) term, and the standard two-electron nonrelativistic Coulomb interaction term,

$$H^{\mathrm{DK+MFSO}}=\sum_i \left(h^{\mathrm{DK}}(i)+h^{\mathrm{MFSO}}(i)\right)+\sum_{i<j}\frac{1}{r_{ij}}. \tag{1}$$

The mean-field spin–orbit Hamiltonian can be written in terms of Pauli matrices as

$$h^{\mathrm{MFSO}}=h_x^{\mathrm{MFSO}}\sigma_x+h_y^{\mathrm{MFSO}}\sigma_y+h_z^{\mathrm{MFSO}}\sigma_z. \tag{2}$$

A more extensive description of the structure of the scalar and spin–orbit operators is given elsewhere,[16,17,20,27] but in the third section we will look in some detail at the MFSO operator used in the present application. The advantage of the one-electron treatment of both scalar and spin–orbit effects through the variationally stable operators mentioned above is that the cost remains comparable to (unrestricted) nonrelativistic Hartree–Fock calculations. This gives computational gain in comparison to four-component methods since the small components of four-spinors and thus additional small-component basis set used for describing of positronic states are eliminated.

Because of the spin–orbit term in the Hamiltonian, we cannot work with spin–orbitals but put electrons into general two-component spinors (two-spinors),

$$|i\rangle=i^{\alpha}\alpha+i^{\beta}\beta. \tag{3}$$

Both components of the spinors are optimized simultaneously in the (two-component) SCF procedure giving $jj/\omega\omega$ characterized electronic states in the presence of the spin–orbit term.

The computational problem is further reduced by (i) enforcing the Kramers symmetry[4,31] on spinors (analogous to the spin-restriction in one-component methods) so that the SCF wave function consists of degenerate Kramers pairs of spinors. (ii) Using the double-group symmetry[4,32,33] of the total Hamiltonian containing the spin–orbit term. One can then construct double group symmetry functions where integrals over Hermitian operators become real quantities even when integrands and functions themselves are complex.[33]

The two-component Kramer's restricted HF method (KRHF) that we use has also been derived by Hafner *et al.*[34,35] Lee and Lee[36] have employed the method by utilizing the relativistic effective core potential (RECP) including the spin–orbit operator. Recently Mosyagin *et al.*[37] applied generalized potentials (GRECP) to simulate the atomic core within a two-component *jj* coupled picture.

III. METHODS AND COMPUTATIONAL DETAILS

The 4-component relativistic code MOLFDIR (Ref. 38) performs Kramer's restricted calculations starting from open/closed shell single determinant HF-SCF and continuing by (Kramers unrestricted) electron correlation methods, like MP2, coupled clusters with iterative treatment of singles and doubles (CCSD) and with inclusion of noniterative triples [CCSD(T), CCSD+T, CCSD-T, see Ref. 9, and references therein] or restricted active space configuration interaction (RASCI).[7] For comparison purposes it, however, also has a nonrelativistic two-component option that forms the basis for the current work.

The MOLFDIR program suite[38] needed only slight modifications to extend its two-component (nonrelativistic) option to the desired quasirelativistic one in which both scalar and spin–orbit relativistic effects can be treated. The changed part of the MOLFDIR was the RELONEL (Ref. 38) program where nonrelativistic one-electron integrals were substituted by their relativistic counterparts taken from the codes listed below.

The DK integrals were extracted from the SEWARD code of the MOLCAS program package.[39] The spin–orbit atomic integrals were obtained from the AMFI code from one of us (B.S.).[40] Both types of integrals were transformed into MOLFDIR double-group irreducible representations[31,33,38] by an interface program that exploits the fact that MOLFDIR atomic basis functions are cubic combinations of Cartesian functions. An independent two-component SCF program in the C_1 symmetry based only on MOLCAS and AMFI integrals was further written to check the MOLFDIR DK(+MFSO) SCF energy values. We note that neglecting the spin–orbit operator in the Hamiltonian Eq. (1) gives energies (for closed-shell systems) identical with those obtained from one-component DK calculations. Within our implementation it is also possible to neglect the spin–orbit operator at the SCF level and include it at the correlated level using SO-CI or QDPT. This can be used to analyze results obtained with these approaches. In our implementation it does not save computer time as the MOLFDIR does not have a specific one-component SCF option. A modification of MOLFDIR similar to our work was done by Lee *et al.*[41,42] for frozen core (RECP) calculations.

Since we use a two-component procedure it would be consistent to generate the atomic mean-field spin–orbit integrals based on atomic two-spinors. This is not possible with the current AMFI integral evaluation code that expects one-component orbitals as input. In this implementation matrix elements over atomic functions of the MFSO operator (without the spin-other orbit part) in Eq. (2) are expressed (after the spin integration) as

$$\langle i|h^{\mathrm{MFSO}}|j\rangle_c = \langle i|h^{\mathrm{SO}}(1)|j\rangle_c + \frac{1}{2}\sum_{\mathrm{M}}^{\mathrm{mf-orbs}} n_M(2\langle iM|h^{\mathrm{SO}}(1,2)|jM\rangle_c - \langle iM|h^{\mathrm{SO}}(1,2)|Mj\rangle_c - \langle Mi|h^{\mathrm{SO}}(1,2)|jM\rangle_c); \quad c=(x,y,z). \tag{4}$$

The two-electron part of the spin–orbit Hamiltonian is thus treated through a summation[27] that runs over occupied (mean-field) spatial $M(l,m_l)$ atomic orbitals. The fixed occupation numbers n_M are in the range 0–2. The orbitals can be defined (i) through the appropriate (general) contractions of the basis set, or (ii) from an interfaced internal atomic SCF code that produce spin–orbit averaged scalar relativistic orbitals for given exponents of the basis set. Method (i) is cumbersome in two-component calculations, because the number of contracted scalar basis functions is necessarily larger than the number of occupied shells, even when using general contraction. This problem, that also appears in the generation of relativistic four-component basis sets, see Refs. 38,43–45, arises from the spin–orbit splitting of the $l>0$ orbitals that requires two separate contractions for each of these shells. This means that the sets (i) and M of Eq. (4) in general do not coincide in the DK+MFSO method and that we need to use the approach (ii).

We have slightly modified the AMFI and the internal atomic SCF programs to be able to perform calculations on a (fractionally) charged atom. In these calculations the occupation numbers used in the mean-field summation can be altered in accordance with the charge.

Further modification of the AMFI for the improved description of the atomic core in the jj-framework is nontrivial and is beyond the scope of the present implementation. Work along these lines is in progress.

Details on systems, examined properties, and basis sets follow in the next paragraphs.

We carried out calculations of spin–orbit splittings of the O_2^+, O_2^-, FO, Cl, and ClO systems following rigorous DCG calculations done previously by one of us (L.V.).[9] We used both decontracted and fully compatible, DK+MFSO recontracted a-pvtz basis sets used in that work, i.e. [16.10.3.2/6.6.3.2] for Cl, [11.7.3.2/5.4.3.2] for F, and [11.7.3.2/5.4.3.2] for O. The reader can find further details there.[9]

As a test case for relativistic effects in heavy systems we took the thallium atom and its hydride for which many reference studies are available in the literature.

For the thallium atom ($^2P_{1/2}$) we calculated the spin–orbit splitting (1/2, 3/2; DK+MFSO, DC) and the first ionization energy (DK, DK+MFSO, and DC) in three different schemes with 13, 19, and 35 correlated electrons. We employed the Wahlgren (scalar) contracted basis,[26] [22.17.14.9/8.7.5.3], the Dyall acvdz relativistic basis set[44] (L:[26.22.15.8/10.13.10.3] S:[22.41.30.15.8/9.17.15.10.3]), its (DK+MFSO) recontracted (large-component) counterpart, and the decontracted basis set supplemented with two g-functions, [24.22.16.10.2].[43,46]

TABLE I. Spin–orbit splitting (in cm^{-1}) of the $^2\Pi_g$ ground state of the O_2^+ molecule. The used distance is 2.1097 a_0. One set of spinors used. 1s spinors frozen.

Method	DK+MFSO (DK+MFSO)[a]	DCG[b]
Reference	233.0 (230.9)	221.8
CCSD	210.5 (209.1)	200.4
CCSD(T)	207.5 (206.3)	197.6
CCSD-T	207.6 (206.3)	197.7
Experiment[c]	197.3	

[a]Decontracted basis set.
[b]Reference 9.
[c]Reference 64.

Calculations of equilibrium geometries r_e, harmonic vibrational frequencies ω_e, dissociation energies D_e, and dipole moments μ_e were performed for the TlH ($X0^+$) molecule. We followed closely four-component calculations of Fægri and Visscher[46] using the same decontracted basis sets[46] [24.22.16.10.2] for Tl and [8.2.1] for H and with the deletion of virtual spinors with energies higher than 10 a.u. The electric dipole moments were calculated here by the finite field method (FFPT) with the electric perturbation of the absolute values 0.0010 and 0.0005 a.u. We neglect picture change effects[47,48] because they are small for valence properties like the electric dipole moment. The perturbed atomic integrals were taken from MOLCAS. The Dunham method[49] was used for evaluation of equilibrium bond distances and of harmonic vibrational frequencies. The counterpoise correction method[50] was used for elimination of the basis set superposition error (BSSE).

Atomic systems were studied in the O_h^* double-group symmetry, homonuclear diatomics in the D_{4h}^* symmetry, and

TABLE II. Spin–orbit splitting (in cm^{-1}) of the $^2\Pi_g$ ground state of the O_2^+ molecule. CCSD(T) and SCF (in parentheses) values. Dependence on the mean-field orbitals and on the 2p occupation number. Contracted basis set.

δ[a] / z[b]	+0.00	+0.50	+1.00
+0	207.5 (233.0)	208.3 (233.8)	209.0 (234.6)
+1	205.1 (230.4)	206.1 (231.5)	207.1 (232.5)
DCG[c]		197.6 (221.8)	
Experiment[d]	197.3		

[a]2p occupation number related to the O^δ system.
[b]Mean-field orbitals calculated for the O^z system.
[c]Reference 9.
[d]Reference 64.

TABLE III. Spin–orbit splitting (in cm^{-1}) of the $^2\Pi_g$ ground state of the O_2^- molecule. The used distance is 2.5511 a_0. One set of spinors used. 1*s* spinors frozen.

Method	DK+MFSO (DK+MFSO)[a]	DCG[b]
Reference	184.4 (184.1)	183.0
CCSD	162.9 (162.9)	161.0
CCSD(T)	159.5 (159.5)	157.4
CCSD-T	159.5 (159.6)	157.5
Experiment[c]	160	

[a]Decontracted basis set.
[b]Reference 9.
[c]Reference 64.

TABLE V. Spin–orbit splitting (in cm^{-1}) of the $^2\Pi$ ground state of the FO molecule. The used distance is 2.5058 a_0. One set of spinors used. 1*s* spinors of the fluorine and of the oxygen frozen.

Method	DK+MFSO (DK+MFSO)[a]	DCG[b]
Reference	183.6 (183.5)	184.9
CCSD	192.5 (192.4)	192.9
CCSD(T)	194.1 (194.1)	194.4
CCSD-T	194.3 (194.3)	194.6
Experiment[c]	193.81	

[a]Decontracted basis sets.
[b]Reference 9.
[c]Reference 65.

heteronuclear molecules in the C_{4v}^* symmetry. The point nuclei model was used in all DK and DK+MFSO computations. All two-component DK+MFSO calculations were carried out with the above mentioned modified MOLFDIR code.[38] One-component DK calculations on Tl were done with the MOLCAS package.[39] DK+MFSO contracted basis sets were prepared with the GENBAS program[38] from the MOLFDIR package.

IV. RESULTS AND DISCUSSION

A. O_2^+, O_2^-, FO, Cl, and ClO

The spin–orbit splittings of the O_2^+, O_2^-, FO, Cl, and ClO systems where molecular orbitals (spinors) are not appreciably changed by relativistic effects are summarized in Tables I–VII. All DK+MFSO values agree very well with the four-component SCF and coupled-cluster DCG results.[9] In general, the mean-field summation should become more sensitive on valence occupation, the smaller the systems. Because two of the systems were charged one could argue that an atomic mean field based on the electron density of a neutral atom is not appropriate. We studied the dependence of the outcome on the valence charge by incorporating a (fractional) charge in the generation of the mean-field orbitals and/or in the mean-field summation of Eq. (4). This is presented in Tables II and IV. It appears that the effect is quite small, which demonstrates the well-known fact that the screening of the nuclear charge that occurs in the spin–orbit operator is dominated by the core orbitals. Relatively more important is which charge is used in the generation of orbitals, and the adaptation of the occupation number in the post-Hartree–Fock mean-field summation is less important. The contracted basis sets give virtually the same result as the uncontracted basis set which proves that contraction can be used, provided that both spin–orbit split components of a shell are treated adequately. Even in a scalar contraction scheme this is not very problematic for these light systems because a few additional *p*-functions suffice.

For heavier atoms substantially larger differences between the DC(DCG) and DK+MFSO treatments of the relativity are expected. We study them in the next sections.

TABLE IV. Spin–orbit splitting (in cm^{-1}) of the $^2\Pi_g$ ground state of the O_2^- molecule. CCSD(T) and SCF (in parentheses) values. Dependence on the mean-field orbitals and on the $2p$ occupation number. Contracted basis set.

δ[a] / z[b]	−1.00	−0.50	+0.00
−1	159.9 (184.9)	160.5 (185.5)	161.0 (186.1)
+0	158.0 (182.9)	158.8 (183.6)	159.5 (184.4)
DCG[c]		157.4 (183.0)	
Experiment[d]	160		

[a]$2p$ occupation number related to the O^δ system.
[b]Mean-field orbitals calculated for the O^z system.
[c]Reference 9.
[d]Reference 64.

TABLE VI. Spin–orbit splitting (in cm^{-1}) of the ^2P state of the chlorine atom. 1*s*, 2*s*, and 2*p* shells of the chlorine frozen.

	2 sets of spinors		1 set of spinors	
Method	DK+MFSO (DK+MFSO)[a]	DCG[a]	DK+MFSO (DK+MFSO)[a]	DCG[b]
Reference	872.2 (871.2)	873.7	887.2 (887.5)	888.9
$3p^5$ correlated electrons				
CCSD	878.6 (878.5)	880.4	889.6 (890.2)	892.1
CCSD+T	874.4 (874.3)	876.3	886.5 (887.0)	889.0
CCSD(T)	874.2 (874.1)	876.1	886.1 (886.6)	888.6
CCSD-T	874.3 (874.2)	876.1	886.2 (886.7)	888.7
$3s^2\ 3p^5$ correlated electrons				
CCSD	810.6 (811.2)	812.3	823.7 (824.7)	826.1
CCSD+T	858.6 (859.5)	860.4	873.1 (874.4)	875.6
CCSD(T)	844.9 (845.7)	846.6	859.0 (860.3)	861.5
CCSD-T	843.7 (844.5)	845.4	857.8 (859.0)	860.3
Experiment[c]	882.4			

[a]Decontracted basis set.
[b]Reference 9.
[c]Reference 51.

TABLE VII. Spin–orbit splitting (in cm^{-1}) of the $^2\Pi$ ground state of the ClO molecule. The used distance is 2.9662 a_0. 1s spinors of the oxygen and 1s, 2s, 2p spinors of the chlorine frozen.

	2 sets of spinors		1 set of spinors	
Method	DK+MFSO (DK+MFSO)[a]	DCG[b]	DK+MFSO (DK+MFSO)[a]	DCG[b]
Reference	222.7 (223.3)	225.2	223.4 (224.0)	225.9
CCSD	299.9 (300.5)	302.6	300.8 (301.4)	303.5
CCSD+T	313.8 (314.7)	316.4	315.9 (316.7)	318.5
CCSD(T)	309.9 (310.7)	312.6	309.7 (310.5)	312.4
CCSD-T	311.8 (312.6)	314.5	312.6 (313.4)	315.3
Experiment[c]			318	

[a]Decontracted basis sets.
[b]Reference 9.
[c]Reference 64.

B. Tl

Thallium represents a good example of the importance of relativistic effects in the theoretical treatment. The energy separation of the $^2P_{1/2}$ and $^2P_{3/2}$ sublevels due to spin–orbit effects amounts to 7793 cm^{-1}, Ref. 51. Calculation of this splitting was the subject of much previous work (Table VIII). For a more extensive overview, see Ref. 5. We first focus on rigorous four-component calculations. Our best calculated DC-SCF value 7643 cm^{-1} is in good agreement with the basis set free value of Rakowitz and Marian[52] of 7640 cm^{-1}. They also report a DC+B-SCF (Breit correction added perturbationally) value of 7499 cm^{-1} which gives us a good estimate for the effect of the omitted Gaunt term in our calculations. Eliav *et al.*[53] performed four-component DC(DCB) Fock-space singles and doubles coupled cluster (RCC) calculations using a very large basis set. They started from the Tl^+ cation and took 35 electrons into correlation. They obtained 7710 cm^{-1} and 7627 cm^{-1} with and without the Breit interaction, respectively.

Han *et al.*[10] have computed splittings of the thallium atom by the two-component RECP method with the modified MOLFDIR code. Their HF, CCSD, CCSD(T) results (Table II in their paper,[10] see also Ref. 5) show the same behavior as our DK+MFSO ones, i.e., a decrease of the splitting by electronic correlation. However, they strongly rely on the quality of pseudopotentials and it is more difficult to find trends of systematic quality improvement of the results.

Failure of perturbative calculations[5,26,52] is primarily caused by different shapes of spin–orbit splitted atomic p spinors. Since we optimize our spinors in the presence of spin–orbit interaction one would expect that our results will be better. This is not always the case as can be read from Table VIII. As expected, the scalar contracted basis set[26] gives poor results differing significantly from those in decontracted and recontracted basis sets. The same holds for the

TABLE VIII. Spin–orbit splitting (in cm^{-1}) of the ^2P ground state of the Tl atom ($^2P_{1/2} \rightarrow {}^2P_{3/2}$).

Method	DK+MFSO	DK+MFSO	DC	DK+MFSO	DC
Basis set	Wahlgren[a]	Dyall[b]		Dyall and Fægri[c]	
SCF	6039	8293	7616	8306	7643
$6s^2\ 5d^{10}\ 6p^1$ correlated electrons					
CCSD	5636	7768	5064	8142	7520
CCSD(T)	5609	7728	4017	8065	7452
$5p^6\ 6s^2\ 5d^{10}\ 6p^1$ correlated electrons					
CCSD				8286	7655
CCSD(T)				8195	7574
$5s^2\ 4f^{14}\ 5p^6\ 6s^2\ 5d^{10}\ 6p^1$ correlated electrons					
CCSD				8324	7690
CCSD(T)				8224	7601
Other theoretical results[d]					
Rakowitz[e]					
DC-SCF					7640
DC+B-SCF					7499
Eliav *et al.*[f]					
DC-SCF					7600
RCC					7710
Rakowitz and Marian[g]					
MC-DC-SCF					7750
Experiment[h]			7793		

[a]Scalar contracted basis set, Ref. 26. Mean-field orbitals taken within contractions. Two sets of spinors.
[b]Acvdz contracted basis set, Ref. 44. One set of spinors.
[c]Decontracted basis set, Ref. 43. Virtual spinors with energies higher than 100 a.u. are deleted. One set of spinors.
[d]For the most recent overview, see Ref. 5.
[e]Reference 66.
[f]Reference 53.
[g]Reference 52.
[h]Reference 51.

TABLE IX. Spin–orbit splitting (in cm^{-1}) of the ^2P ground state of the Tl atom. Only $p-p$ excitations are allowed.

Method[a]	Active spinors	DK+MFSO	DC[b]
QDPT		6465	6499
SOCI-10	$6p$	7366	7412
SOCI-100	$6p$	8550	8613
SOCI-All	$6p$	14744	14741
SOCI-All	$5p6p$	10290	10298
SOCI-All	$4p5p6p$	8841	8851
SOCI-All	$3p4p5p6p$	8016	8028
SOCI-All	$2p3p4p5p6p$	7441	7454
Full	$6p$	8306	7643
Experiment[c]		7793	

[a]SOCI-X: SO-CI calculations allowing single excitations to spinors with energies below X a.u. SOCI-All: Single excitations to all p spinors. Full: Hartree–Fock step done in the presence of the spin–orbit term.
[b]Visscher and Saue, Ref. 59.
[c]Reference 51.

ionization energy (Table X). However, Gagliardi *et al.*[12] calculated splitting of 7565 cm^{-1} in the same basis set using the two-component density functional theory and with the same (DK+MFSO) Hamiltonian. DFT $j-j$ coupled treatment most probably compensates the inadequacy of scalar contracted basis sets and causes the increase of the splitting from our SCF value of 6039 cm^{-1} by about 1500 cm^{-1}.

Somewhat surprising is, however, the poor performance of the DC method in conjuction with the contracted Dyall basis set.[44] Upon correlating 13 electrons the decrease in splitting due to the electronic correlation is much larger than in the DK+MFSO approach and gives a value significantly below the experimental value. This is probably due to the inadequacy of the contraction scheme to describe the full correlation of the d-shell. It is puzzling that the effect in the DK+MFSO scheme is so much smaller. In the uncontracted basis set the results are much better. Here one sees that the absolute magnitude of the correlation energy is larger but that the basis set allows for a more balanced description of both states which leads to a smaller effect on the observed splitting. Still, the convergence with increasing correlation space and basis set is rather slow and our best CCSD(T) value for the 35 electron calculations should be regarded as a lower limit for this method. The DK+MFSO method gives a systematic overestimation of the DC-value that cannot be attributed to the missing Gaunt interaction in the DC-calculations (according to Rakowitz and Marians results discussed above the DCG values should be an additional 140 cm^{-1} lower).

This overestimation can partly be explained by going to the traditional DK approach in which spin–orbit effects are not included in the orbital generation step. This is a follow up on earlier work by one of us (L.V.),[54] where it was predicted that a pseudovariational collapse should occur also with the DK+MFSO Hamiltonian. This is indeed what we, and independently also Fagerli and Saue,[55] observed in the SO-CI calculations of Table IX. The results give also a clue to the cause of the overestimation of the SO-splitting observed in the two-component DK+MFSO calculations because there is no such overestimation in the perturbative and SO-CI calculations. This means that it is not primarily the difference in Hamiltonians (DK+MFSO vs DC) that causes the overestimation of spin–orbit splitting but rather the use of one-component orbitals in the mean-field summation. If we would be able to use optimized two-component spinors in this summation than the result of the DK+MFSO Hamiltonian and the full DC result should be close because we apply it to the same atom as used to define the mean-field. The relaxation of the orbitals with the fixed MFSO-operator brings the splitting from the PT-value of 6465 cm^{-1} to a value of 8306 cm^{-1}, while full relaxation of both orbitals and mean field should give something closer to the DCB Hartree–Fock value of 7499 cm^{-1}.

TABLE X. The first ionization energy (in cm^{-1}) of the Tl atom ($^2P_{1/2} \rightarrow {}^1S_0$).

Method	DK	DK+MFSO	DK+MFSO	DC	DK+MFSO	DC
Basis set	Wahlgren[a]		Dyall[b]		Dyall and Fægri[c]	
SCF	39 691	43 263	45 899	45 096	45 971	45 184
$6s^2\ 5d^{10}\ 6p^1$ correlated electrons						
CCSD	41 771	45 292	47 596	48 632	48 539	47 802
CCSD(T)	42 038	45 410	47 682	49 398	48 582	47 855
$5p^6\ 6s^2\ 5d^{10}\ 6p^1$ correlated electrons						
CCSD					48 655	47 910
CCSD(T)					48 710	47 976
$5s^2\ 4f^{14}\ 5p^6\ 6s^2\ 5d^{10}\ 6p^1$ correlated electrons						
CCSD					48 703	47 954
CCSD(T)					48 757	48 021
Other theoretical results						
Eliav *et al.*[d]						
DC-SCF						45 100
RCC						49 279, 48 575
Experiment[e]					49 264	

[a]Scalar contracted basis set, Ref. 26. Mean-field orbitals are taken within contractions. Two sets of spinors.
[b]Acvdz contracted basis set, Ref. 44. One set of spinors.
[c]Decontracted basis set, Ref. 43. Virtual spinors with energies higher than 100 a.u. are deleted. One set of spinors.
[d]Reference 53.
[e]Reference 67.

TABLE XI. Molecular properties of the TlH.

Property / Method	r_e (Å)	ω_e (cm^{-1})	D_e (eV)	μ_e (D)
DK+MFSO[a]				
SCF	1.859	1465	1.15	−0.80
14 correlated electrons				
CCSD(T)	1.867	1398	1.97	−1.03
36 correlated electrons				
CCSD(T)	1.865	1383	1.95	
Other theoretical results[b]				
Fægri and Visscher[c]				
DC-SCF	1.870	1447		
14 correlated electrons				
DC-CCSD(T)	1.876	1385	2.00	
36 correlated electrons				
DC-CCSD(T)	1.874	1371	1.98	
DCG-CCSD(T)[d]	1.877	1376	2.06	
Seth *et al.*[e]				
DC-SCF	1.869	1454	1.17	−0.94
14 correlated electrons				
DC-CCSD(T)	1.885	1376	2.07	−1.22
Experiment[f]	1.868	1391	2.06	

[a]The two-component values are fully compatible with the four-component listed below under item b except the d. Dipole moments calculated at own optimized distances.
[b]For the overview of calculations until 1998, see Ref. 5.
[c]Decontracted basis sets. Virtual spinors with energies higher than 10 a.u. are deleted in BSSE corrected correlated calculations, Ref. 46.
[d]BSSE corrected results are in smaller contracted basis sets, Ref. 46.
[e]No BSSE correction, Ref. 56.
[f]Reference 68.

Results of one-, two-, and four-component SCF, CCSD, and CCSD(T) calculations of the first ionization energy (IE) of thallium atom are presented in Table X. Here the two-component results are all in very good concordance with the DC ones.

Eliav *et al.*[53] obtained excellent results with a four component Fock space coupled cluster method, 49 280 cm^{-1}, when starting from four-spinors of the Tl^+ cation. His DHF value 45 100 cm^{-1} matches with our value of 45 184 cm^{-1}, while our CC values are somewhat lower. This is probably mostly due to the smaller basis set employed in our calculations.

C. TlH

The TlH molecule has been studied theoretically many times (see Ref. 5, and references therein). Destabilization of chemical bond due to spin-orbit effects was recognized in early days of relativistic quantum chemistry. In the jj coupling picture, what is relevant for qualitative description of the atom, the weakening of the thallium hydrogen bond is caused by the large fraction of π character in the bonding $6p_{1/2}$ spinor of Tl.

Results of molecular properties r_e, ω_e, D_e, and μ_e together with other (four-component[45,46]) theoretical and experimental values are presented in Table XI. Correspondence with the four-component counterparts[46] is retained. Douglas–Kroll relativistic effects make the bond shorter by about 1 pm at the SCF level, and weaker at both uncorrelated and correlated levels with respect to the DC (DCG) outcomes. As for electric properties the two-component dipole moments agree with Seth's[56] values; the decrease of the TlH polarity (which is $Tl^{\delta+}H^{\delta-}$) by spin–orbit effects is larger in the DK+MFSO investigation.

TABLE XII. Comparison of timings (in seconds) in two- and four-component calculations. TlH molecule. Decontracted basis sets, 36 correlated electrons.

Program[a]	DK+MFSO[b]	DC[c]
RELTWEL	391 (0.086)	4 538
MFDSCF	1 822 (0.059)	30 801
ROTRAN	44 689 (0.256)	174 265
RELCCSD	19 724 (1.038)	19 002
Total	66 626 (0.291)	228 606

[a]The MOLFDIR package (Refs. 38,9) was executed by one 375 MHz Power3 processor on one node of an IBM Nighthawk system.
[b]Fraction of the four-component DC timings in parentheses.
[c]SS two-electron integrals discarded.

The influence of spin–orbit effects on molecular properties was estimated recently also by pseudopotential calculations,[41,57] we decided to leave out this study here, because the comparison is less-straightforward than with other all-electron calculations.

The CPU resources required to perform the time-consuming parts of the calculations are given in Table XII. It is clear that the current implementation gives better timing than a full DC-calculation if the process is dominated by the integral generation and Hartree–Fock steps. Overall the DK+MFSO calculation takes about 29% of the time necessary for a DC calculation in the framework of the MOLFDIR package.

V. CONCLUSIONS

The proposed two-component Kramers restricted DK+MFSO approach where both scalar and spin–orbit effects are employed in the spinor space formation is a computationally cheaper alternative to the four-component Dirac–Coulomb–(Gaunt/Breit) based methods. Specifically contracted basis sets are recommendable for this type of calculations. Largest sources or errors in comparison to the accurate DC(DCG) treatment of relativity are because of the mean-field one-center approximation of spin–orbit effects and because of the specific Douglas–Kroll reduction of the full DCB Hamiltonian. The restriction of AMFI to fixed one-component mean-field orbitals leads to overestimation of the spin–orbit splitting in the Tl and causes probably also the bond weakening observed in the TlH relative to the corresponding Dirac–Coulomb studies. For light elements the use of one-component orbitals does not lead to noticeable errors.

Further improvements of the DK+MFSO method can be envisioned along the lines of (i) rigorous adaptation of the mean-field part of the AMFI operator in a jj coupled framework to obtain a better screening of the one-electron spin–orbit part, (ii) replacement of the Douglas–Kroll terms by other transformed Hamiltonians that cover relativistic effects up to higher orders of α,[58–60] and (iii) interfacing to the KR MCSCF (Ref. 61) and CI (Ref. 25) methods, connection to

the Fock space coupled clusters method.[62,63] This and other developments of two/four-spinor based *ab initio* correlation methods can bring useful tools for relativistic quantum chemistry in the 21st century.

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